



PATENT

Attorney's Docket No.: U 012119-9

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231



NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of Inventors:

1. RAGHUNATH VITTHAL CHOUDHARI
2. RENGASWAMY JAGANATHAN
3. SOPAN TUKARAM CHAUDHARI
4. CHANDRASHEKHAR VASANT RODE

WARNING: The Declaration must name all of the actual inventor(s).

For (title):

AN IMPROVED PROCESS FOR THE PREPARATION OF COPPER CHROMITE CATALYST

1. Type of Application

This new application is for a(n) (check one applicable item below):

- ☒ Original (nonprovisional)
☐ Design
☐ Plant

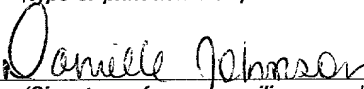
WARNING: Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4) unless the International Application is being filed as a divisional, continuation or continuation-in-part application.

CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this New Application Transmittal and the documents referred to as enclosed therein are being deposited with the United States Postal Service on this date **FEBRUARY 24, 1999** in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EJ405329134US addressed to the: Assistant Commissioner of Patents, Washington, D.C. 20231

DANIELLE JOHNSON

(type or print name of person mailing paper)


(Signature of person mailing paper)

NOTE: Each paper or fee referred to as enclosed herein has the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 CFR 1.10(b).

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 CFR 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

WARNING: Do not use this transmittal for the filing of a provisional application.

2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach **ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED**.

WARNING: If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.

WARNING: When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional **must** be filed prior to the Saturday, Sunday or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).

- ☐ The new application being transmitted claims the benefit of prior U.S. application(s) and enclosed are **ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED**.

NOTE: If one of the following 3 items apply, then complete and attach **ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED** and a **NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION**.

- ☐ Divisional.
☐ Continuation.
☐ Continuation-in-Part (C-I-P).

3. Papers Enclosed That Are Required For Filing Date Under 37 CFR 1.53 (Regular) or 37 CFR 1.153 (Design) Application

10 Pages of specification

3 Pages of claims

1 Pages of Abstract

 Sheets of drawing

- ☐ formal
☐ informal

WARNING: **DO NOT** submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. Comments on proposed new 37 CFR 1.84. Notice of March 9, 1988 (1990 O.G. 57-62).

NOTE: "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page." 37 C.F.R. 1.84(c).

(complete the following, if applicable)

- ☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)". 37 C.F.R. 1.84(b).

4. Additional papers enclosed

- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement (37 CFR 1.98)
- ☐ Form PTO-1449
- ☐ Citations
- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other

5. Declaration or oath

- ☐ Enclosed
- executed by *(check all applicable boxes)*
- ☐ inventors.
- ☐ legal representative of inventors. 37 CFR 1.42 or 1.43
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
- ☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. *See item 13 below for fee.*
- ☒ Not Enclosed.

WARNING: *Where the filing is a completion in the U.S. of an International Application but where a declaration is not available or where the completion of the U.S. application contains subject matter in addition to the International Application the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

- ☒ Application is made by a person authorized under 37 CFR 1.41(c) on behalf of *all the above named inventors*. (The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently).

NOTE: *It is important that all the correct inventor(s) are named for filing under 37 CFR 1.41(c) and 1.53(b).*

- ☐ Showing that the filing is authorized. *(Not required unless called into question. 37 CFR 1.41(d).)*

6. Inventorship Statement

WARNING: *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.*

The inventorship for all the claims in this application are:

- ☐ The same
- ☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

7. Language

NOTE: An application including a signed oath or declaration may be filed in a language other than English. A verified English translation of the non-English language application and the processing fee of \$130.00 required by 37 CFR 1.17(k) is required to be filed with the application or within such time as may be set by the Office. 37 CFR 1.52(d).

NOTE: A non-English oath or declaration in the form provided or approved by the PTO need not be translated. 37 CFR 1.69(b).

- ☒ English
☐ non-English
☐ the attached translation is a verified translation. 37 CFR 1.52(d).

8. Assignment

- ☒ An assignment of the invention to COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.
☒ will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

WARNING: A newly executed "CERTIFICATE UNDER 37 CFR 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993. 1150 O.G. 62-64.

9. Certified Copy

Certified copy of application

Country	Appln. No.	Filed
INDIA	NOT YET KNOWN	FEBRUARY 12, 1999
from which priority is claimed		
<input type="checkbox"/> is attached.		
<input checked="" type="checkbox"/> will follow.		

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. Fee Calculation (37 CFR 1.16)

- A. ☒ Regular Application

Claims as Filed

Number Filed	Number Extra	Rate	Basic Fee 37 CFR 1.16(a) \$760.00
Total Claims (37 CFR 1.16(c))	6 - 20 = 0 x \$	18.00	
Independent Claims (37 CFR 1.16(b))	2 - 3 = 0 x \$	78.00	
Multiple dependent claim(s), if any (37 CFR 1.16(d))	+ \$	260.00	

- ☐ Amendment cancelling extra claims enclosed.
- ☐ Amendment deleting multiple-dependencies enclosed.
- ☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d).

Filing Fee Calculation \$

- B. ☐ Design application
(\$310.00 — 37 CFR 1.16(f))

Filing Fee Calculation \$

- C. ☐ Plant application
(\$480.00 — 37 CFR 1.16(g))

Filing Fee Calculation \$

11. Small Entity Statement(s)

- ☐ Verified Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is(are) attached or has been filed.

Filing Fee Calculation (50% of A, B or C above) \$

NOTE: Any excess of the full fee paid will be refunded if a verified statement and a refund request are filed within 2 months of the date of timely payment of a full fee. 37 CFR 1.28(a).

12. Request for International-Type Search (37 CFR 1.104(d)) (Complete, if applicable)

- ☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made At This Time

- ☒ Not Enclosed

☒ No filing fee is to be paid at this time. (This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently.)

- ☐ Enclosed

☐ basic filing fee \$

- ☐ Recording assignment
(\$40.00; 37 CFR 1.21(h)) (See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION.")
- ☐ Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached.
(\$130.00; 37 CFR 1.47 and 1.17(h)) \$
- ☐ For processing an application with a specification in a non-English language.
(\$130.00; 37 CFR 1.52(d) and 1.17(k)) \$
- ☐ Processing and retention fee
(\$130.00; 37 CFR 1.53(d) and 1.21(l))
- ☐ Fee for international-type search report
(\$40.00; 37 CFR 1.21(e)). \$

NOTE: 37 CFR 1.21(l) establishes a fee for processing and retaining any application which is abandoned for failing to complete the application pursuant to 37 CFR 1.53(d) and this, as well as the changes to 37 CFR 1.53 and 1.78, indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid or the processing and retention fee of § 1.21(l) must be paid within 1 year from notification under § 53(d).

Total fees enclosed \$

14. Method of Payment of Fees

- ☐ Check in the amount of \$
- ☐ Charge Account No. 12-0425 in the amount of \$

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).

15. Authorization to Charge Additional Fees

WARNING: If no fees are to be paid on filing, the following items should not be completed.

WARNING: Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

- ☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 12-0425.
 - ☐ 37 CFR 1.16(a), (f) or (g) (filing fees)
 - ☐ 37 CFR 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

- ☐ 37 CFR 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)
- ☐ 37 CFR 1.17 (application processing fees)

WARNING: While 37 CFR 1.17(a), (b), (c) and (d) deal with extensions of time under § 1.136(a), this authorization should be made only with the knowledge that: "Submission of the appropriate extension fee under 37 C.F.R. 1.136(a) is to no avail unless a request or petition for extension is filed." (Emphasis added). Notice of November 5, 1985 (1060 O.G. 27)

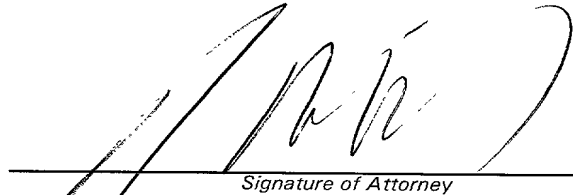
- ☐ 37 CFR 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).

NOTE: 37 CFR 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application ... prior to paying, or at the time of paying, ... issue fee". From the wording of 37 CFR 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

16. Instructions As To Overpayment

- ☐ credit Account No. 12-0425
☐ refund



Signature of Attorney

Reg. No. 31,053

Tel. No. (212) 708-1915

John Richards
Ladas & Parry
26 West 61 Street
New York, NY 10023

- ☐ **Incorporation by reference of added pages**

(Check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

- ☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added ____

- ☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added ____

- ☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added ____

- ☒ **Statement Where No Further Pages Added**

(If no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item:)

- ☒ This transmittal ends with this page.

Field of invention

This invention relates to a process for the preparation an improved copper chromite catalyst useful for hydrogenation of diethyl maleate (DEM) to tetrahydrofuran (THF) with very high selectivity. More particularly, it relates to a process for the preparation of an improved copper chromite catalyst with uniform composition and specific characteristics containing copper, chromium zinc and aluminium as catalyst components. The catalyst thus prepared is then calcined according to the procedure described here and this catalyst has the specific characteristics such as surface area, porosity, particle density. The process of the present invention could be used by catalyst manufacturers and producers of tetrahydrofuran. The catalyst system comprises of the mixed oxides of copper, chromium, aluminium and zinc to give high selectivity of tetrahydrofuran over longer period of time. The used catalyst can be regenerated and reused again.

Background of invention

In the prior art, the use of copper chromite catalyst is described for its catalytic activity for the hydrogenation of dicarboxylic acids or dicarboxylic acid esters and /or anhydrides. Most of these patents use copper chromite catalysts containing the combination of one or more mixed oxides of copper, zinc, barium, aluminium of varying composition. Such catalysts have been procured from the catalyst manufacturers. U.S. Patent No. 4,810,807, (1989) describes the hydrogenation of butyl ester of maleic anhydride using a copper chromite catalyst commercially available from United Catalysts (No. T-2107). The patent also mentions the use of a cocatalyst consisting of oxides of copper, chromium and barium available from Harshaw/Filtrol (No. 1107T).

The U.S. Patent 4, 584,419 (1986) and the International Patent W086/03189 (1986)

use the most preferred catalysts which contain copper and chromium together in a range of 60-62% and no more than approximately 15% by weight of stabilizers (i.e. barium and/or manganese) The method of catalyst preparation is not clearly understood from these literature, however, the reduction of the copper chromite has been described in International patent WO 86/03189 (1986).

Recently, Castiglioni et al. (Chemistry and Industry, 5 July 1993,) have reported preparation of copper chromite catalyst by using sodium carbonate as precipitating agent. Also, the copper chromite catalysts mentioned in this paper do not contain aluminium and zinc together, and the side products such as butanol etc. obtained are in high quantities.

Objects of the invention

In the present invention we propose the preparation method for an improved copper chromite catalyst of a particular composition and with specific physical characteristics for hydrogenation of diethyl maleate to give highest selectivity of tetrahydrofuran. The catalyst composition is uniform and this eliminates the use of a cocatalyst or different catalyst zone. Also, the stability of the catalyst is tested for continuous hydrogenation for more than 630 hours and it was found that it was not necessary to add a stabilizer to the catalyst system. The catalyst is calcined in three steps with varying temperatures. The catalyst can also be regenerated and used again for the hydrogenation of diethyl maleate to THF.

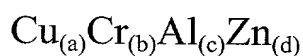
It is therefore an object of the present invention to provide an improved copper chromite catalyst of uniform composition and specific characteristics for giving better activity and selectivity in vapour phase hydrogenation of diethyl maleate.

It is another object of the present invention to provide a method for preparation of an improved copper chromite catalyst of uniform composition and specific characteristics for giving better activity and selectivity in vapour phase hydrogenation of diethyl maleate.

Summary of the invention

The present invention discloses a novel copper chromite catalyst useful for the hydrogenation of diethyl maleate to tetrahydrofuran with a very high selectivity. The catalyst is characterized by a uniform composition and specific characteristics such as surface area, porosity and particle density and comprises of mixed oxides of copper, chromium, aluminium and zinc. It is prepared by making an aqueous mixture of solutions of a source of copper, a source of aluminium and a source of zinc and adding to this mixture a source of chromium. The resultant precipitate is separated and calcined under specific conditions of temperature and pressure to obtain the product. The catalyst has a life of more than 630 hours with constant activity. The used catalyst can also be regenerated to match the original hydrogenation activity.

Accordingly, the present invention provides an improved copper chromite catalyst having the molar composition



Wherein

- a = 10 – 40 mole %
- b = 10 – 40 mole %
- c = 10 – 30 mole %
- d = 5 – 40 mole %

and $a + b + c + d = 100$

and characterised by XRD pattern as shown in table 1

Table I: XRD analysis of the copper chromite catalyst

θ	Intensity (%)
18	100
26.2	100
27.4	48

35.8	92
44.2	48
56.6	44

The present invention also provides a process for the preparation of the above-mentioned catalyst which comprises preparing aqueous solutions of source of copper, a source of aluminium and a source of zinc, adding to this mixture a solution of source of chromium, under stirring conditions to obtain the precipitate, separating the precipitate by conventional methods, drying the precipitate at a temperature ranging between 80 to 110 °C, calcining the dried material in static air at a temperature ranging between 200 to 500 °C for a period ranging between 2 to 5 hrs., to obtain the product.

In a preferred embodiment the source of copper is a salt of copper selected from nitrate, sulfate, acetate or chloride, preferably, copper nitrate.

In yet another embodiment the source of aluminium is an aluminium salt selected from nitrate, chloride, or aluminium oxide, preferably, aluminium nitrate.

In yet another embodiment the source of zinc is a salt of zinc selected from nitrate, or zinc sulfate or chloride, or zinc oxide, preferably, zinc nitrate.

In yet another embodiment the source of precipitating agent is an ammonium salt selected from ammonium dichromate or ammonium chromate, preferably ammonium dichromate.

In a feature of the present invention the catalyst prepared as per the procedure described in examples is required to be calcined under static air in a muffle furnace at 200°C for one hour, 300 °C for one hour and at 400 °C for two hours. Before carrying out hydrogenation experiments, the catalyst is to be activated *in situ* in the reactor. This is done

under a steady flow of hydrogen at a temperature 80 to 230°C. The most preferred temperature is 175-200 °C. The activation can be done with pure hydrogen or hydrogen diluted with an inert like nitrogen. The pressure of activation can be between 1-30 atmospheres. The most preferred pressure of activation is 5-15 atmospheres. The catalyst should be activated for a period of 200 hours. The most preferred activation period is 100 hours.

The process of the present invention results in an improved copper chromite catalyst of the particular composition and specific characteristics for giving better activity and selectivity in vapour phase hydrogenation of diethyl maleate.

The process of the invention is described herein below with examples, which are illustrative only and should not be considered to limit the scope of the invention.

The experiments were carried out in a single tube reactor of 19 mm diameter. In a typical experiment the catalyst was charged approximately in the middle portion of the reactor tube. The space above and below the catalyst was packed with inert corborundum beads. The reactor was heated by electric furnaces. The liquid feed (DEM) and hydrogen were introduced near the top of the reactor. The inert zone over the top of the catalyst serves as a preheater for the reactants. The product stream leaving the reactor is cooled to condense the liquid products.

Example-1:

An improved copper chromite catalyst was prepared by the following procedure. A mixture of 302 gm of copper nitrate, 281.5 gm of aluminium nitrate and 149 gm of zinc nitrate was dissolved in 2000 ml of distilled water. A solution of ammonium dichromate was prepared by dissolving 315 gms of ammonium dichromate in 1500 ml distilled water and adding dropwise approximately 220 ml of 30 % aqueous ammonia solution. The solution of

nitrate was stirred while the ammonium chromate solution was poured into it in a thin stream. Stirring was continued till the addition was completed after which a reddish brown precipitate was obtained. This precipitate was filtered and dried in a oven at 110 °C. This dry precipitate was then calcined in a muffle furnace for one hour at 200°C , one hour at 300 °C and two hours at 400 °C. The dry copper chromite catalyst thus obtained was pelletized and stored in bottles.

The catalyst composition before calcination and reduction is : Cu + Cr = 50 mol %, Zn = 20 mol %, Al = 30 mol %.

The reactor was packed with 30 gms of the catalyst prepared as per the procedure discribed above. This was activated insitu under a continuous flow of hydrogen at 150°C for two hours, at 200°C for 24 hours and at 200°C and 10 bar pressure for 48 hours. Pure hydrogen gas was used at a flow rate of 10 NI/hr. After the activation the hydrogenation of diethyl maleate reaction was carried out and the XRD analysis was carried out in the usual manner. The selectivity of tetrahydrofuran was tested and was found to be \cong 90%.

Example-2:

In this example, a copper chromite catalyst was prepared by the following procedure. A mixture of 48.33 gm of copper nitrate and 18.8 gm of aluminium nitrate was dissolved in 200 ml of distilled water. A solution of ammonium dichromate was prepared by dissolving 31.5 gms of ammonium dichromate in 150 ml distilled water and adding dropwise approximately 25 ml of 30 % aqueous ammonia solution. The solution of nitrate was stirred while the ammonium chromate solution was poured into it in a thin stream. Stirring was continued till the addition was completed after which a reddish brown precipitate was obtained. This precipitate was filtered and dried in a oven at 110 °C. This dry precipitate was then calcined in a muffle furnace for one hour at 200°C , one hour at 300 °C and two hours at

400 °C. The dry copper chromite catalyst thus obtained was pelletized and stored in bottles.

The catalyst composition before calcination and reduction is : Cu + Cr = 80 mol % and Al = 20 mol %. After the activation of the catalyst the hydrogenation of diethyl maleate reaction was carried out as described earlier. The selectivity of tetrahydrofuran obtained was < 30 % and there was formation of undesirable side products.

Example-3:

In this example, a copper chromite catalyst with different composition was prepared by the following procedure. A mixture of 105.7 gm of copper nitrate and 55.77 gm of zinc nitrate was dissolved in 500 ml of distilled water. A solution of ammonium dichromate was prepared by dissolving 78.75 gms of ammonium dichromate in 375 ml distilled water and adding dropwise approximately 55 ml of 30 % aqueous ammonia solution. The solution of nitrate was stirred while the ammonium chromate solution was poured into it in a thin stream. Stirring was continued till the addition was completed after which a reddish brown precipitate was obtained. This precipitate was filtered and dried in a oven at 110 °C. This dry precipitate was then calcined in a muffle furnace for one hour at 200°C , one hour at 300 °C and two hours at 400 °C. The dry copper chromite catalyst thus obtained was pelletized and stored in bottles.

The catalyst composition before calcination and reduction is : Cu + Cr = 70 mol % and Zn = 30 mol %. After the activation of the catalyst the hydrogenation of diethyl maleate reaction was carried out as described earlier. The selectivity of tetrahydrofuran obtained was < 25 % and there was formation of undesirable side products.

Example-4:

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664220"8072960

In this example the catalyst was prepared by dissolving 151 gms of copper nitrate 500 ml distilled water. A solution of ammonium dichromate was prepared by dissolving 78.75 gms of ammonium dichromate in 375 ml distilled water and adding dropwise approximately 55 ml of 30 % aqueous ammonia solution. The solution of nitrate was stirred while the ammonium chromate solution was poured into it in a thin stream. Stirring was continued till the addition was completed after which a reddish brown precipitate was obtained. This precipitate was filtered and dried in a oven at 110 °C. This dry precipitate was then calcined in a muffle furnace for one hour at 200°C , one hour at 300 °C and two hours at 400 °C. The dry copper chromite catalyst thus obtained was pelletized and stored in bottles.

The catalyst composition before calcination and reduction is : $\text{Cu} + \text{Cr} = 100 \text{ mol } \%$. After the activation of the catalyst the hydrogenation of diethyl maleate reaction was carried out as described earlier. The selectivity of tetrahydrofuran obtained was $< 20 \%$ and there was formation of undesirable side products.

Example-5:

In this example, a copper chromite catalyst with different composition was prepared by the following procedure. A mixture of 24.91 gm of copper nitrate, 31.65 gm of aluminium nitrate 12.08 gm of zinc nitrate, and 22.05 gms of barium nitrate was dissolved in 250 ml of distilled water. A solution of ammonium dichromate was prepared by dissolving 39.37 gms of ammonium dichromate in 190 ml distilled water and adding dropwise approximately 30 ml of 30 % aqueous ammonia solution. The solution of nitrate was stirred while the ammonium chromate solution was poured into it in a thin stream. Stirring was continued till the addition was completed after which a reddish brown precipitate was obtained. This precipitate was filtered and dried in a oven at 110 °C. This dry precipitate was then calcined in a muffle furnace for one hour at 200°C, one hour at 300 °C and two hours at 400 °C. The dry copper

chromite catalyst thus obtained was pelletized and stored in bottles.

The catalyst composition before calcination and reduction is : Cu + Cr = 33 mol %, Ba = 27 mol %, Zn = 13 mol % and Al = 27 mol %. After the activation of the catalyst, the hydrogenation of diethyl maleate reaction was carried out as described earlier. The selectivity of tetrahydrofuran obtained was < 25 % and there was formation of undesirable side products.

Example-6:

In this example, a copper chromite catalyst with different composition was prepared by the following procedure. A mixture of 60.4 gm of copper nitrate, 37.51 gm of aluminium nitrate 29.75 gm of zinc nitrate, and 13.07 gms of barium nitrate was dissolved in 400 ml of distilled water. A solution of ammonium dichromate was prepared by dissolving 63.0 gms of ammonium dichromate in 300 ml distilled water and adding dropwise approximately 45 ml of 30 % aqueous ammonia solution. The solution of nitrate was stirred while the ammonium chromate solution was poured into it in a thin stream. Stirring was continued till the addition was completed after which a reddish brown precipitate was obtained. This precipitate was filtered and dried in a oven at 110 °C. This dry precipitate was then calcined in a muffle furnace for one hour at 200°C, one hour at 300 °C and two hours at 400 °C. The dry copper chromite catalyst thus obtained was pelletized and stored in bottles.

The catalyst composition before calcination and reduction is : Cu + Cr = 50 mol %, Ba = 10 mol %, Zn = 20 mol % and Al = 20 mol %. After the activation of the catalyst, the hydrogenation of diethyl maleate reaction was carried out as described earlier. The selectivity of tetrahydrofuran obtained was \cong 54 %.

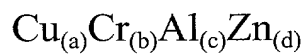
The main advantages of the invention are as follows:

- i. There is no use of sodium bicarbonate in the preparation of the catalyst by the present process of the invention.

- ii. The copper chromite catalyst prepared by the process of present invention shows no loss of its catalytic activity and selectivity in hydrogenation of diethyl maleate to tetrahydrofuran for a long period (atleast for 630 hours).
- iii. The copper chromite catalyst prepared by the process of present invention has a particular composition which gives very high conversion and selectivity of tetrahydrofuran in hydrogenation of diethyl maleate.
- iv. There is a thorough mixing of catalyst component elements forming a homogeneous mixture of the catalyst precursors, which on calcination yields copper chromite catalyst with uniform composition of catalyst components.
- v. All the catalyst components are in the oxide form due to the calcination procedure used in the process of present invention.

WE CLAIM:

1. An improved copper chromite catalyst having the molar composition



wherein

- a = 10 – 40 mole %
- b = 10 – 40 mole %
- c = 10 – 30 mole %
- d = 5 – 40 mole %

and $a + b + c + d = 100$

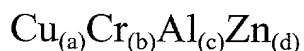
and characterised by XRD pattern as shown in table 1

Table I: XRD analysis of the copper chromite catalyst

θ	Intensity (%)
18	100
26.2	100
27.4	48
35.8	92
44.2	48

56.6	44
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2. A process for the preparation of an improved copper chromite catalyst having the molar composition



wherein
a = 10 – 40 mole %
b = 10 – 40 mole %
c = 10 – 30 mole %
d = 5 – 40 mole %

and $a + b + c + d = 100$

and characterised by XRD pattern as shown in table 1

Table I: XRD analysis of the copper chromite catalyst

θ	Intensity (%)
18	100
26.2	100
27.4	48
35.8	92
44.2	48
56.6	44

which comprises preparing aqueous solutions of source of copper, a source of aluminium and a source of zinc, adding to this mixture a solution of source of chromium, under stirring conditions to obtain the precipitate, separating the precipitate by conventional methods, drying the precipitate at a temperature ranging between 80 to 110 °C, calcining the dried material in static air at a temperature ranging between 200 to 500 °C for a period ranging between 2 to 5 hrs., to obtain the

product.

3. A process as claimed in claim 1 wherein, the source of copper may be salts of copper such as nitrate, sulfate, acetate or chloride, preferably copper nitrate.
4. A process as claimed in claim 1, wherein the source of aluminium may be aluminium salts such as nitrate, chloride, or aluminium oxide preferably aluminium nitrate.
5. A process as claimed in claim 1, wherein the source of zinc may be salts of zinc such as nitrate, or zinc sulfate or chloride, or zinc oxide, preferably zinc nitrate.
6. A process as claimed in claim 1, wherein the source of precipitating agent may be ammonium salt such as ammonium dichromate or ammonium chromate, preferably ammonium dichromate

ABSTRACT

The present invention provides a process for the preparation of an improved copper chromite catalyst for the hydrogenation of diethyl maleate to tetrahydrofuran with very high selectivity. This invention particularly relates to a process for the preparation of an improved copper chromite catalyst with specific composition and physical properties containing copper, chromium, zinc and aluminium as catalyst components in order to achieve selective production of tetrahydrofuran via single step hydrogenation of diethyl maleate. The calcination procedure has also been described to achieve the best activity. The catalyst has a life of more than 630 hours with constant activity. The used catalyst can also be regenerated to match the original hydrogenation activity.